

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C11D 1/62, 1/50, 3/48, A01N 33/02	A1	(11) International Publication Number: WO 00/14193 (43) International Publication Date: 16 March 2000 (16.03.00)
(21) International Application Number: PCT/GB99/02773 (22) International Filing Date: 6 September 1999 (06.09.99) (30) Priority Data: 9819397.2 7 September 1998 (07.09.98) GB (71) Applicant (for all designated States except US): MACGRE- GOR, Keith, Martin [GB/GB]; P.O. Box 2, Ilkley, West Yorkshire LS29 9YB (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): GIBBS, Anthony, Marston [GB/GB]; 19 Grange Close, Ludham, Great Yarmouth, Norfolk NR29 5PZ (GB). (74) Agent: APPELYARD LEES; 15 Clare Road, Halifax HX1 2HY (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COMPOSITION FOR THE REMOVAL OF BIOLOGICAL AND ORGANIC SUBSTANCES		
(57) Abstract The present invention relates to a composition for and an improved method of removing all types of biologically-generated soiling. The invention is concerned with the removal of the biological source of the soiling without resorting to the type of chemical activity generally associated with disinfection. In particular the invention concerns the removal from surfaces of algae and similar organisms, including many organisms which secrete substances for purpose of securing the organism to a surface.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**Composition for the removal of biological and organic
substances**

5 The present invention relates to a composition for and an improved method of removing all types of biologically-generated soiling. The invention is also concerned with the actual removal of the biological source of the soiling without resorting to the type of chemical activity generally associated with disinfection.

10

The present invention relates in particular to the removal from surfaces of algae and similar organisms, including many organisms which secrete substances for purpose of securing the organism to a surface.

15

The compositions of the present invention serve to modify these biological secretions. Biological substances which are secreted by certain organisms, together with organic and other inorganic substances, form the basis of the
20 adhesion of an organism whether it be micro, macro or larger to surfaces. This adhesion makes it difficult for traditional methods of removal of the organism from the surface to be totally effective. As a result, the quality of hygiene treatments or other subsequent
25 treatments following to the removal of surface contamination from biological sources is reduced greatly.

Common methods of removing biologically generated soils generally require the use of a suitable surface active
30 agent. Additives are generally included in known preparations for the purpose of improving the soil-

lifting properties of the surface active agent.

Other known preparations have conventionally employed cell toxins which are commonly described as disinfectant
5 agents. These substances have very little or no actual activity in releasing such organisms from a surface. Hence, although the cells are destroyed many will remain on a contaminated surface thereby providing nutrients for further colonisation by a subsequent contaminant.

10

However, a number of problems arise when using traditional compositions, and although these may be minimised by devising suitable formulations, the result is often a compromise in terms of the cleaning
15 properties, safety or ease of use. Conventional agents may be highly toxic and/or corrosive thereby presenting a hazard to the user and requiring the use of specialist protective clothing. Certain treatments may be subject to statutory limitations to their use or be only suitable
20 for professional application. Containment of the cleaning agent only to the desired area may therefore also be an issue. This is particularly relevant where biological or other complex organic contamination is present and aggressive or corrosive agents have
25 traditionally been required.

Whilst the toxin or other cell inhibitor present in conventional preparations may well have a wide spectrum of activity and thus be effective, there is the problem
30 that areas adjacent to that being treated may need to be protected or other safety precautions may be necessary to

prevent the spread of the toxic and/or corrosive agent. This represents both an increased risk and cost when using such agents.

5 In addition, there are certain areas in which highly aggressive cleaning agents simply would not be compatible with the environment in which they are required, for example the use of most toxin-containing cleaning formulations would be a health hazard in algae removal
10 from around swimming pools, paths and patios, occupied buildings or the like. These areas are all touched or subject to human or animal contact.

The present invention seeks to provide an effective
15 cleaning composition which is not aggressive or corrosive and does not pose a hazard to the user or to the external environment. The composition is also intended to be economical to manufacture and easy to use without any special training or equipment. It is also an aim to
20 provide a treatment which ideally is able to prevent the re-occurrence of contamination at a treated site.

The present invention achieves these various aims and overcomes the difficulties inherent in the prior art
25 using formulations which address the way in which the unwanted contamination such as an organism is secured to a surface.

According to the present invention, there is provided a
30 composition comprising:

- (i) an alkyl or aryl amine, or an amine donor selected from: a Group III metal-amino chelate, lauryl dimethyl benzyl ammonium chloride (BAC) or cetyl trimethyl ammonium bromide;
- 5 (ii) a complexing agent selected from: an oxazole, a thiazole, an isoxazole, an isothiazole; and biguanide polymer;
- (iii) a Group III B element selected from Al, Ga or In the form of a salt or complex ion;
- 10 (iv) a carrier; and optionally
- (v) a d-block element in the form of a salt or complex ion; and
- (vi) a viscosity modifier and/or a catalyst.

Immobile organisms rely on surface adhesion for security
15 and life support and thus multiplication. The composition of the present invention is effective against surface contamination by both breaking the bond between the contaminant and the surface, and by directly attacking the contaminant itself, thereby preventing its
20 continual propagation.

The invention provides a broad spectrum micro-organism and macro-organism cell release mechanism. In cases, and with specific reference to algal and similar cells, removal will provide sufficient treatment to ensure the
25 biological safety of a surface with regard to contamination or health. In many cases, the compositions of the present invention also serve to inhibit cell

development in addition to ensuring their removal from the surface.

Where a further degree safety i.e sterility of the surface is required, the release of microbic cells from a surface using the compositions of the present invention allows traditional disinfection or sterilisation treatment to be more effective. The reason is that any organic matter which would normally reduce the anti-microbic activity of a disinfectant will no longer be present in the case of surface treatment with compositions according to the present invention.

A composition comprises the above complexing agents and may include auxiliary complexing agents. Such auxiliary complex agents may be salts of transition elements, for example of copper with an organic acid such as lactic, citric or ascorbic acids.

Algal cell-release compositions of the invention may thus comprise a complexing agent(s) selected from one or more salts of an organic acid and a transition metal, a salt of a group III metal or a d-block metal salt, a carrier capable of assisting wetting preferably a non-ionic or amphoteric surfactant, and a cationic moiety wherein the moiety is part of a chemically-independent compound or chemically associated with the carrier or complexing agent.

Preferably, the amine donor is lauryl dimethyl benzyl ammonium chloride, benzalkonium chloride or cetyl trimethyl ammonium bromide. The amine donor may be in the form of a free base or a salt. When an amine is

provided as component (i), whether in place of or in addition to the amine donor, the amine is preferably a lower alkyl amine having one or more alkyl substituents each being C₆ or less, or a single aryl substituent and 0, 1 or 2 alkyl substituents of C₆ or less. The amine may be in the form of a free base or a salt.

The complexing agent is preferably 1, 2 benzisothiazolin-3-one, 2-methyl-4, 5-trimethylene-4-isothiazolin-3-one, or polymeric biguanide hydrochloride.

10 The Group III B element may be in the form of a salt or in the form of a metal amino chelate of that salt. The Group III B element is preferably aluminium. Aluminium chloride or aluminum amino chelates, such as aluminium amino sulphate, are particularly preferred. If the Group
15 III B element is metal amino chelate then components (i) and (iii) of the composition may be identical, or they may be different components of the composition.

The component containing the d-block element is not essential to the effective working of the formulations of
20 the present invention. However, by including both a Group III B element and a d-block element a substantial improvement in efficacy may be noted. In particular, the component containing the d-block element improves the activity against soils secreted by algae and the like.

25 Preferred d-block elements, when present, include iron, copper, manganese and zinc. Copper is particularly preferred.

Preferably, the salts of the Group III B element or the d-block element contain halo, sulphate, nitrate, citrate,

tartrate, or oxalate anions. However, any salt which is stable and soluble in water will suffice.

The carrier is inert with respect to reaction with the other components of the formulation and may be water or a
5 suitable organic solvent such as methanol, ethanol, ethylene glycol or isopropanol or a mixture containing some or all of the above-mentioned solvents. Isopropanol in combination with water is particularly preferred. The carrier may also be a conventional cationic or non-ionic
10 surfactant, or an aromatic ester in aqueous solution.

Typical carriers for solid and powder formulations include simple solid alkali carbonates and polyphosphates, or cross-linked polyacrylates or other
15 inert material such as pumice dust or wood flour. The carrier may also be in the form of a complex silicate salt (formulations containing complex silicates can be used to treat new concrete or other materials of construction thereby rendering such surfaces algae
20 repellent).

In an embodiment of the invention, the composition may be absorbed into a porous matrix of carrier material to increase surface area of the composition or to control
25 the release of the composition.

Alternatively, salts of at least one component of the composition may have a reduced solubility in the carrier so that the rate of release can be controlled as
30 required.

The composition in accordance with the present invention may be provided in a liquid, gel, solid or powder form.

As an optional feature, the compositions of the present invention, when in liquid or gel form, may also include a conventional viscosity modifier such as cellulose or xanthan gum in order to make the composition easier to handle and use.

As an optional feature, the compositions of the present invention may also include a catalyst.

Preferably, the catalyst is an immobilised biological catalyst which functions to further reduce the cell adhesion to a surface.

The composition of the present invention preferably comprises based on 100% activity, by weight:

2 to 50%, and more preferably 5 to 8% inclusive, of the alkyl or aryl amine, or the amine donor;

0.1 to 10%, and more preferably 0.5 to 1.0% inclusive, of the complexing agent;

25

0.05 to 4%, and more preferably 0.05 to 0.50%, inclusive of the salt or complex ion of the Group III B element;

0.05 to 4%, and more preferably 0.05 to 0.50%, inclusive, of the d-block element when present; and

30

up to 10%, inclusive, of additives when present;

with the balance of the composition comprising the carrier.

5

Within the scope of the above mentioned ranges, the proportions may be varied to suit particular conditions or requirements.

- 10 The compositions of the present invention, whether in liquid, gel, solid or powder form, provide a concentrate for dilution prior to application. From 10 to 100 mls of a liquid or gel formulation is diluted in 1000 mls of water for application to a surface. In the case of solid
15 or powder formulations, from 5 to 50 gms of the composition is dissolved in 1000 mls of water for application to a surface.

The precise mechanism whereby the compositions of the
20 present invention operate is not presently understood. However, it is thought that the composition reduces the adhesion between microbic cells and the surface.

In particular, it is believed that the compositions
25 target secretions from macro-organisms such as algal cells. This reduces the ability of the cells to absorb nutrients and thus the cells weaken and can be removed easily by mechanical means and can be more effectively destroyed by traditional methods such as disinfectants.

30

In some cases, the compositions may exert a direct

cytotoxic effect on the organisms in situ in addition to performing the function of removing the organism from the surface. On some surfaces there also appears to be a residual effect after treatment which further reduces the development or re-contamination of a treated surface. This is a significant advantage of the compositions of the present invention since frequent treatment is therefore not necessary. The compositions of the present invention also have the benefit of reducing noxious odours associated with certain secretions from microorganisms. The treatment can thus provide effective odour control in many cases.

The following compositions which are effective against algal contamination and the like are presented by way of example only.

Example 1

An aqueous formulation for subsequent dilution prior to application to a surface was prepared from the following components, expressed as % by weight:

	lauryl dimethyl benzyl ammonium chloride	4.1%
25	2-methyl-4, 5-trimethylene-4-isothiazolin-3-one	0.37%
	aluminium ammonium sulphate	2.4%
	copper citrate	3.5%
	non-ionic surfactant	0.5%
	isopropyl alcohol	5.0%
30	deionised water	to 100%

Example 2

An aqueous formulation for subsequent dilution prior to application to a surface was prepared from the following
5 components, expressed as % by weight:

	benzalkonium chloride	6%
	aluminium chloride	0.06%
	polymeric biguanide hydrochloride	0.60%
10	sodium benzoate	0.05%
	isopropyl alcohol	3.0%
	deionised water	to 100%

The concentrated aqueous formulations were diluted with
15 water, in the ratio of 50 mls of concentrate per 1000 mls of water, and applied to an external paved area test site on which extensive algal contamination had been cultivated. The adhered algae was easily lifted by rinsing with water or brushing following the application
20 of the diluted formulation to the whole area. No recontamination with algae had appeared six months after treatment.

CLAIMS

1. A composition comprising:
 - 5 (i) an alkyl or aryl amine, or an amine donor selected from: a Group III metal-amino chelate, lauryl dimethyl benzyl ammonium chloride (BAC) or cetyl trimethyl ammonium bromide;
 - (ii) a complexing agent selected from: an oxazole, a
10 thiazole, an isoxazole, an isothiazole; and biguanide polymer;
 - (iii) a Group III B element selected from Al, Ga or In the form of a salt or complex ion;
 - (iv) a carrier; and optionally
 - 15 (v) a d-block element in the form of a salt or complex ion; and
 - (vi) a viscosity modifier and/or a catalyst.
2. A composition as claimed in claim 1 further comprising a salt of a transition element with an
20 organic acid as an auxiliary complexing agent.
3. A composition as claimed in claim 1 or 2, wherein the amine donor is lauryl dimethyl benzyl ammonium chloride, benzalkonium chloride or cetyl trimethyl ammonium bromide.
- 25 4. A composition as claimed in claim 1 or 2, wherein an amine is provided as component (i) in place of or in

addition to the amine donor and the amine is a lower alkyl amine having one or more alkyl substituents each being C₆ or less, or a single aryl substituent and 0, 1 or 2 alkyl substituents of C₆ or less.

- 5 5. A composition as claimed in any preceding claim, wherein the complexing agent is 1, 2 benzisothiazolin-3-one, 2-methyl-4, 5-trimethylene-4-isothiazolin-3-one, or polymeric biguanide hydrochloride.
- 10 6. A composition as claimed in any preceding claim, wherein the salt or complex ion of the Group III B element is aluminium chloride or aluminium amino sulphate.
- 15 7. A composition as claimed in any preceding claim, wherein the d-block element is selected from the group comprising: iron, copper, manganese and zinc.
8. A composition as claimed in any preceding claim which comprises by weight based on 100% activity:
- 20 2 to 50%, and more preferably 5 to 8% inclusive, of the alkyl or aryl amine, or the amine donor;
- 0.1 to 10%, and more preferably 0.5 to 1.0%, inclusive, of the complexing agent;
- 0.05 to 4%, and more preferably 0.05 to 0.50%, inclusive, of the salt or complex ion of the Group
- 25 III B element;
- 0.05 to 4%, and more preferably 0.05 to 0.50%, inclusive, of the d-block element when present; and

up to 10%, inclusive, of additives when present;
with the balance of the composition comprising the
carrier.

5 9. A liquid or gel composition as claimed in any
preceding claim diluted with from 10 to 100 parts of
water.

10 10. A solid or powder composition as claimed in any of
claims 1 to 8, diluted with water so that each 1000
mls of the diluted composition contains from 5 to 50
gms of the solid or powder.

11. A method of removing algae from a surface, the
method comprising the steps:

- (a) diluting the composition of any of claims 1 to
8 with water to produce a diluted composition;
- 15 (b) applying the diluted composition to the
surface;
- (c) optionally applying mechanical force to the
surface; and
- (d) rinsing the diluted composition and algae from
20 the surface with water.

12. A method as claimed in claim 11, wherein one part of
a liquid or gel composition is diluted with from 10
to 100 parts of water.

25 13. A method as claimed in claim 11, wherein a solid or
powder composition is diluted so that 1000 mls of

the diluted composition contain from 5 to 50 gms of the solid or powder.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB 99/02773

A. CLASSIFICATION OF SUBJECT MATTER

C11D1/62, C11D1/50, C11D3/48, A01N33/02

According to International Patent Classification (IPC) or to both national classification and IPC 7

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D, A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI, Week 198912, Derwent Publications Ltd., London, GB; Class A01N33/04, AN 1989-090795; & JP 01 042406 A (NITTO BOSEKI CO. LTD.) 14 February 1989, abstract.</p> <p>--</p>	1, 3
A	<p>DATABASE WPI, Week 198506, Derwent Publications Ltd., London, GB; Class A01N35/04, AN 1985-034303; & JP 59 227805 A (KUMIAI CHEM IND CO LTD) 21 December 1984, abstract.</p>	1, 2, 5, 7

☒ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search
25 November 1999

Date of mailing of the international search report

14.01.2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 631 epo nl.
Fax (+31-70) 340-3016

Authorized officer

SEIRAFI e.h.

INTERNATIONAL SEARCH REPORT

Inter national Application No
PCT/GB 99/02773

-2-

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<div style="text-align: right;">--</div> EP 0542199 A (LONZA INC.) 19 May 1993, claims.	1,9-13
A	<div style="text-align: right;">--</div> US 5173110 A (STOVICEK) 22 December 1992, abstract.	1
A	<div style="text-align: right;">--</div> EP 0542489 A (ROHM AND HAAS COMPANY) 19 May 1993, the whole document. <div style="text-align: center;">----</div>	1,5

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

FCT/GB 99/02773 SAE 248300

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
in no way liable for these particulars
which are given merely for the purpose
of information.

La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
dans le rapport de recherche inter-
national visée ci-dessus. Les renseigne-
ments fournis sont donnés à titre indica-
tif et n'engagent pas la responsabilité
de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
JP A2	1042406	14-02-1989	keine - none - rien	
JP A2	59227805	21-12-1984	JP B4	3070681
EP A1	542199	19-05-1993	AT E	133030
			AU A1	245111/92
			AU B2	650366
			BR A	9203727
			CA AA	2082368
			CA C	2082368
			DE C0	49207725
			DE T2	69207725
			EP B1	542199
			ES T3	2083058
			JP A2	6036607
			JP B4	7037361
			NO A0	923909
			NO A0	923909
			ND A	245078
			NZ A	5290805
			US A	5290805
			ZA A	9207085
			US A	5413722
US A	5173110	22-12-1992	AU A1	29687/89
			AU B2	618070
			CA A1	1336993
			CA A	1035836
			CA B	1017087
			EP A1	528335
			IL A0	89226
			IL A1	89226
			JP A2	2070769
			NO A0	890494
			NO A	890494
			ZA A	8900939
			US A	4990547
			US A	5096488
EP A2	542489	19-05-1993	CA AA	2082840
			EP A3	542489
			IL A0	103706
			IL A1	103706
			JP A2	5246807
			ZA A	9208764